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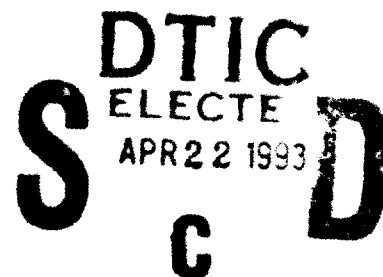


OFFICE OF NAVAL RESEARCH

FINAL TECHNICAL REPORT

GRANT N00014-90-J-1569

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A. Synthesis of Oligoimides and Oligoimide Anion Radicals. Key to the results described in parts B-D are compounds based on naphthalene dianhydride (**A**) and dimethoxybenzidine (**B**). It was demonstrated that **AB** type oligoimides with lengths up to 80 **A** (8nm) (**BABABABAB**) could be synthesized as single molecular weight, pure and usually soluble compounds.^{6,7,16} Although rotation about the single bonds along the chain is possible, the chains cannot fold. These oligomers constitute the longest, single molecular weight rigid rods that are known. Various end groups could be attached and unsymmetrical rigid rods (different end groups) could be prepared. The compounds were characterized by NMR, IR, MS and HPLC. In one case a single crystal was obtained which confirmed the linear structure and that the **B** units were twisted with respect to the **A** units.

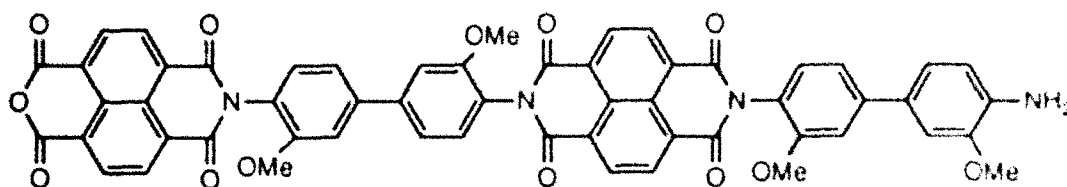
Electrochemical studies showed that the naphthalene diimide group (**A**) formed anion radicals (**A⁻**) and dianions (**A⁼**), which were stable in DMF in the absence of air. In **BABABAB** oligomers one or two electrons could be reversibly added to each **A** unit. Significantly **A⁻** was extremely stable in aqueous solution.

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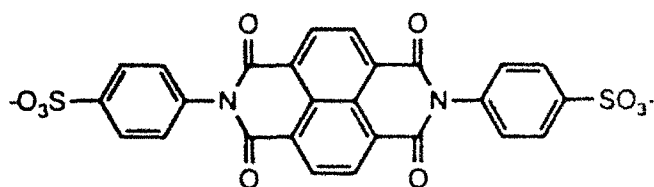
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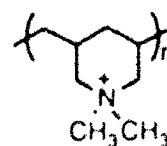
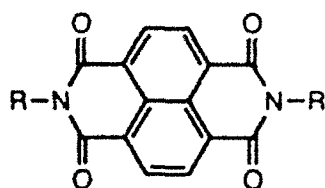
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A - B - A - B



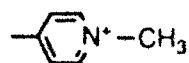
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2⁺

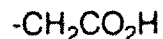
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R Groups

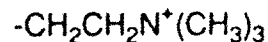
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b



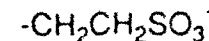
c



d



e



f



B. Anion Radical π -Stacks in Solution. This study documented for the first time the evolution of π -stacks from monomer to dimer to solution phase stack to the solid state. Diimide **1** was reduced to form **1⁻**, which was shown to be monomeric in DMF, dimeric in water and π -stacked in aq NaCl (Scheme 1).^{8,10} ΔH and ΔS for the monomer-dimer equilibrium was measured. Stacking was identified from the anisotropic ESR signal and the "optical conduction band" found in the NIR, which was displaced to longer wavelengths under conditions known to favor aggregation, e.g. added divalent cations or low concentrations of polycations, like **2⁺**. As discussed below these stacks can be precipitated to form anisotropic solids, which have similar spectra.

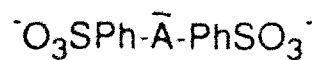
The idea of having "conducting" aggregates in a solution is an intriguing one and we have now prepared a number of water soluble substituted imides (3) analogous to 1. Key observations made when these imides were reduced with dithionite in water are: (1) The "dication-anion radical" $3a^{\cdot-}$ forms stacks (1800 nm) even in the absence of added salt. Stacks of $3a^{\cdot-}$ are formed independently of the presence of neutral $3a$, which remains monomeric in water. These results indicate that the anion radicals prefer to self dimerize and stack, not make mixed dimers or stacks with neutral. (2) Anion radical $3b^{\cdot-}$ dimerizes in water, but does not form stacks. When precipitated with the polymeric polycation 2^+ only dimers are present. Clearly the end group is critical for determining stacking vs. dimerization.

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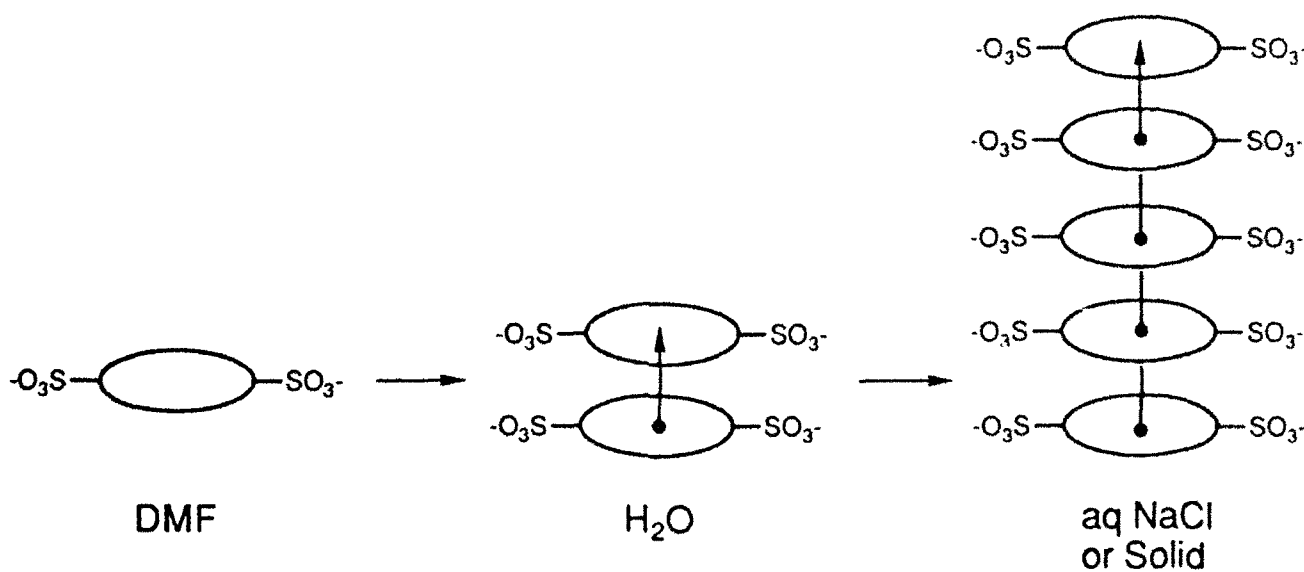
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Evolution of a Solid State Structure.

π -Stacks in Solution.



	<u>λ_{MAX} (nm)</u>	<u>ESR (Spin Count)</u>	<u>Structure</u>
DMF	780	Isotropic (96%)	Monomer
H ₂ O	1140	Isotropic (4%)	Dimer
H ₂ O, NaCl	1700	Anisotropic	π -Stack
Solid	>2000	Anisotropic	π -Stack



C. An Anisotropic Conducting Polymer. Recently, advantage has been taken of the solution phase π -stacking of 1^+ to prepare thick films of $1^+/2^+$.^{1,9} Electrochemical reduction of 1 in aqueous solutions of the film forming polycation 2^+ precipitated a film containing both. Using a mercury pool cathode a method was developed to prepare large ($40\text{ cm}^2 \times 0.5\text{ mm}$) free standing films. ESR and optical spectra demonstrate that the films are anisotropic and contain π -stacks of 1^+ preferentially oriented along the film plane. The conductivity is highly anisotropic with $\sigma=10^{-2}$ along the film plane and 10^{-7} across the film plane. It is proposed that the anisotropy results because the stacks assemble in solution and precipitate with the large dimension along the electrode plane. Because the films are air stable (even though they are n-doped) and so anisotropic they are quite interesting. A patent application has been submitted.

These films are also unusual in that they rapidly and reversibly take up water from the air leading to a 10^3 change in electronic conductivity. The temperature dependence of the hydrated films shows that the conductivity activation energy of hydrated films is 0.3 eV. This corresponds well with the optical conduction band wavelength. A third unexpected aspect is the temporal dependence of the conductivity. Briefly, using 4-probes we observe that when the current on the outer electrodes is stepped, the voltage on the inner electrodes is initially quite high, but drops with time. This is in the wrong direction for polarization. When the current is reversed a similar voltage change in the reverse direction is observed. This rules out heating effects and suggests that the applied field leads to a morphological change which improves the conductivity.

D. Langmuir Blodgett^{2,6,12} and Self Assembled Thin Films.^{7,13}

Eleven oligoimides with lengths up to 8 nm and various end groups have been used to make Langmuir Blodgett films. After compression to make stable layers on the trough, horizontal lifting was used to reproducibly make multilayer films on several substrates. Spectroscopic studies, especially grazing angle IR, attenuated total reflectance IR and angle resolved XPS, demonstrated that several oligomers, e.g., $^-\text{O}_3\text{SPh-A-B-A-PhSO}_3^-$, gave highly anisotropic films in which the average long axis of the molecules lay some 15° above the surface plane. It was further demonstrated using aq. Ca^{2+} electrolyte that the films could be electrochemically reduced on gold without desorption and that the reduced films contained dimerized anion radicals.

This work is significant because it demonstrates that the LB method can be used to form non-amphiphilic rigid rods into anisotropic multilayer structures. The

particular thin films have special relevance because of the wide spread use of polyimide films in microelectronics.

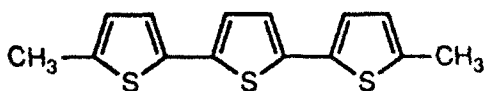
Self assembled monolayers were formed on gold from several thiol terminated oligomers (**HSPH-ABABABAB/Au** was featured on the cover of Langmuir). GIB and XPS confirmed the structure. Electrochemistry was used to demonstrate that each **A** unit was electroactive and that up to 8 electrons per molecule could be added without desorption. These studies established for the first time that thiophenol groups were good binding agents for gold and that cathodic reactions were possible without disruption of the binding. In contrast to the LB films there was no evidence for interactions between the anion radicals in the film. Indeed it seems clear that counteranions readily insert between the tethered chains. Rate constants for interfacial electron transfer were measured. The electroactivity was also employed to determine the rate of adsorption.

E. Cation Radical π -Dimers of Oligothiophenes. Our intent was to characterize cation radicals and dications of oligothiophenes in solution as models for polarons and bipolarons in conducting oxidized polythiophene. Recent studies have focused on 2,5"-dimethylterthiophene (**4**).⁴ It was chosen because the methyl groups should block the normal polymerization mechanism of the cation radical.

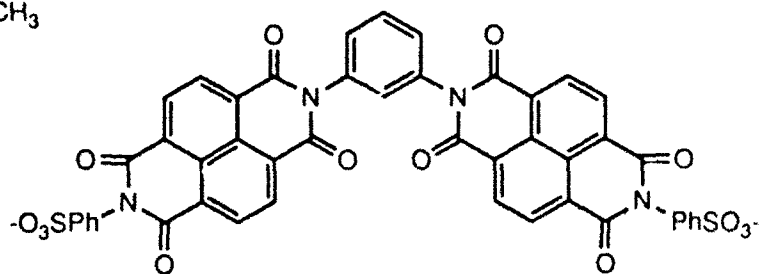
Spectroelectrochemical studies done jointly with Kent Mann of this department showed that this pure oligomer undergoes reversible oxidation in CH_3CN producing cation radicals. On the time scale of minutes polymerization does not proceed. ESR and optical spectra reveal that the cation radical is present as a monomeric species at low concentration and a dimeric species, which we assign to a π -dimer, at higher (5 mM) concentration. By varying the temperature ΔH and ΔS for the equilibrium could be calculated.

Since the π -dimer is ESR silent, we propose that it is a structural alternative to the bipolaron. This suggests that π -dimers and π -stacks form in solid oxidized polythiophene and that conductivity along such stacks is a mechanism worthy of careful consideration. Since we have previously shown that some oligomeric salts have conductivities nearly as high as the conducting polymer it would appear that long single chain conjugation lengths are unnecessary.

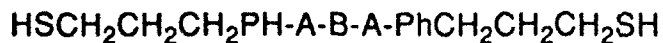
Two other blocked terthiophenes and a blocked bithiophene have also been studied. They give cation radicals which show the same type of spectral changes indicative of dimerization. Monomeric cation radicals have two π - π^* bands, π -dimers show these two bands shifted to lower wavelength plus a charge transfer band in the NIR. At high concentration there is the suggestion of further aggregation. Further coulometric oxidation produces the dications as not very stable species. The spectra of the dications (bipolarons) have single π - π^* bands in the visible. We have determined that one of the few previous literature reports on oligothiophene cations contains a misassignment.



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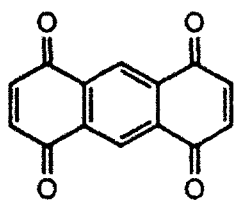
F. Patterned Surface Structures, STM It has been a long standing goal of this project to construct molecular patterns on surfaces through synthesis. The approach has been to synthesize rigid molecules with known dimensions and shapes; to attach these molecules to surfaces; and to image them on the surface. Extensive progress has been made on the synthesis of molecular lines, i.e. pure rigid rods of known length up to 8.0 nm and on "Y" shaped molecules, e.g. **5**. We have also developed methods for the attachment of rods to SiO₂ and gold surfaces. Using STEM on a molecular line derivatized with Ir₄(CO)₁₁, we were able to measure the length of an organic molecule with a microscope for the first time. This is not an appropriate method for imaging complex shapes, however, and we have been hopeful for some time that STM would be the solution.

Suggestions that polypyrrole on graphite could be imaged with STM, led to us to pursue this method for imaging organic molecules. This work was not brought to a successful conclusion. Our STM studies of polypyrrole suggested that the images were likely to be artifactual. Our skepticism has been mirrored by others and the problems with interpretation of STM images of single molecules (especially on graphite) have been documented. Current studies of rigid rod oligomers with two thiol tethers, e.g. **6** to gold are promising, but still inconclusive. We hypothesize that on gold these oligomers will not be disturbed by the tip and that they will be detected. Their distinctive shape and precise length should be observable.

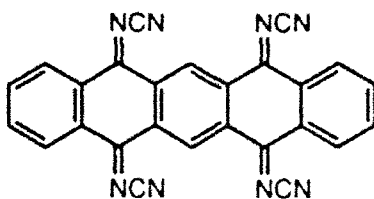
G. NIR Dyes and Anion Radical Photophysics At the beginning of this grant period we had discovered that several diquinone anion radicals had electronic transitions in the near infrared (NIR). Anion radical **7**⁻, for example, had an intense band at 1560 nm. Because there are to our knowledge no organic dyes that absorb beyond about 1300 nm it was of interest to prepare an analog of **7**⁻ that would be air stable. This was accomplished by preparing the N-cyanoimine derivative **8**⁻. As expected from the reduction potential for **8** (E⁰=0.10 V, SCE) this anion was quite air stable and it had maximum absorbance at 1520 nm (ε=15,000).^{11,14} Several analogs have been prepared illustrating that this approach can lead to a family of dyes which absorb at various wavelengths between 1-2 microns. A patent application has been submitted.³

Based on studies¹⁵ of crystals of **7**⁻ and extensive studies of the conductivity of cyanoimine derivatives of monoquinones it was of interest to examine the solid state properties of **3**⁻. The IR spectrum of pure **8**⁻, Na⁺ showed an optical conduction band, as well as Fano bands from coupling of the CN vibration and the "optical conduction"

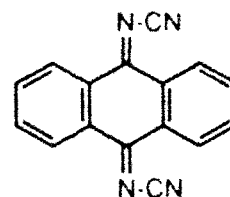
band. The pressed pellet conductivity of 8^- , Na^+ , $\sigma=0.5 \text{ S cm}^{-1}$, is substantially higher than typical values for simple anion radical salts. Thus, we contend that anion radicals with low lying excited states may be better conductors than otherwise expected.



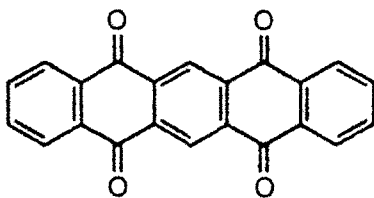
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On the theoretical side, *ab initio* calculations have been used, but in addition and quite usefully, we have demonstrated that PPP calculations on neutral molecules give excellent predictions of E° , ESR coupling constants and optical transition energies for quinone and imide anion radicals.⁵

These studies of anion radicals as dye molecules revealed how little is known about the spectroscopy and photophysics of these species. We had previously proposed to study electron transfer reactions of electronically excited anion radicals, but when experiments of this kind were undertaken an unexpected result was observed. Professor Paul Barbara and coworkers performed femtosecond pump-probe measurements on six anion radicals formed in DMF solution. The ions e.g. 8^- , 9^- , 10^- , were chosen to absorb light at 800 nm, the wavelength of excitation and detection. In each case it was determined that there was an extremely rapid relaxation. Excited state lifetimes were 100-500 fs. To our knowledge only three anion radicals have been reported to fluoresce and we have shown that one of these is artifactual. Since there have been many studies of electrochemiluminescence

which involve ion radical precursors we suspect that they usually do not emit and that is because they have extremely short lifetimes.

In contrast to the non-emission from anion radicals we have established that diimide dianions, e.g. 12^- emit from π^* states with quantum yields of about 0.1. In this series both the neutral and dianion emit, but the anion radical does not. This suggests that the odd electron spin is important for the rapid relaxation process, perhaps through spin-orbit coupling.

ONR Supported Publications (1990 - Present)

1. Patent applied for: Anisotropic Conducting Polymer. L.L. Miller and C.J. Zhong, 1992.
2. L. Atanasoska, V. Cammarata, B.J. Stallman, W.S.V. Kwan, and L.L. Miller, "Langmuir-Blodgett Films of Rigid Rod Oligoimides on Gold: An X-Ray Photoelectron Spectroscopy Study," *Surf. Interface Anal.*, **1992**, *18*, 163.
3. Patent applied for: Near Infrared Dyes and Method of Forming a Film Capable of Absorbing in the Near Infrared Region. L.L. Miller and C.A. Liberko, 1991.
4. M.G. Hill, K.R. Mann, L.L. Miller, and J.F. Penneau, "Oligothiophene Cation Radical Dimers. An Alternative to Bipolarons in Oxidized Polythiophene," *J. Am. Chem. Soc.*, **1992**, *114*, 2728.
5. C.A. Liberko, S.F. Rak, and L.L. Miller, "PPP-MO Calculations Predict Spectra of Quinone and Imide Anion Radicals," *J. Org. Chem.*, **1992**, *57*, 1379.
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7. W.S.V. Kwan, L. Atanasoska, L.L. Miller, "Oligoimide Monolayers Covalently Attached to Gold," *Langmuir*, **1991**, *7*, 1419.
8. J.F. Penneau, B.J. Stallman, P. Kasai and L.L. Miller, "An Imide Radical Which Dimerizes and Assembles into π -Stacks in Solution," *Chem. Mat.*, **1991**, *3*, 791.
9. C.J. Zhong, B. Zinger, V. Cammarata, P. Kasai and L.L. Miller, "A Conductive, Anisotropic Polymer Film Formed by Electroprecipitation of π -Stacks of an Imide Anion Radical and a Polycation," *Chem. Mat.*, **1991**, *3*, 787.
10. J.F. Penneau and L.L. Miller, "An Imide Anion Radical Which Assembles into π -Stacks in Solution," *Angew. Chemie*, **1991**, *30*, 987.
11. S.F. Rak, C.A. Liberko and L.L. Miller, "Mixed Valence in Conjugated Anion Radicals. Solution and Solid State Studies," *Synth. Metals*, **1991**, *42*, 2365.

12. V. Cammarata, C.J. Kolaskie, L.L. Miller and B.J. Stallman, "Rigid Rod Oligoimides Form Oriented Langmuir Blodgett Films," *Chem. Commun.*, **1990**, 18, 1290.
13. W.S.V. Kwan, J.F. Penneau and L.L. Miller, "ESR and Electrochemical Study of Self Assembled Oligoimide Monolayers on Gold," *J. Electroanal. Chem.*, **1990**, 291, 295.
14. L.L. Miller and C.A. Liberko, "Near Infrared Dyes. An Air Stable Radical Anion," *Chemistry of Materials* **1990**, 2, 339.
15. M.W. Forkner, L.L. Miller and S.F. Rak, "The Structure of a Conductive, Diamagnetic Diquinone Radical Anion Salt," *Syn. Metals*, **1990**, 36, 65.
16. T.M. Dietz, B.J. Stallman, W.S.V. Kwan, J.F. Penneau and L.L. Miller, "Soluble Oligoimide Molecular Lines Which Have Persistent Poly(anion-radicals) and Poly(dianions)," *Chem. Commun.*, **1990**, 5, 367.
17. L.L. Miller, "Molecular Lines," NATO Conference on Lower Dimensional Materials and Molecular Electronics.